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14. ABSTRACT
This proposal requests the purchase of a RHK Technology ATM 300 Ambient Environment Scanning Tunneling Microscope (STM) for atomic- and molecular-resolution imaging of soft biological and polymeric materials under ambient and liquid conditions. The proposed instrument will be housed in the Center for Nano- and Molecular Science and Technology at The University of Texas at Austin (UT-Austin), where it will be accessible 24 hrs a day, 365 days a year, for hands-on materials characterization and experiments conducted by student, postdoctoral, and faculty researchers from multiple colleges and academic departments around campus, as well as to outside

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Report Title

Final Report: Multi-Functional Scanning Probe Microscope for Atomic Resolution Imaging of Soft Surfaces and Interfaces

ABSTRACT

This proposal requests the purchase of a RHK Technology ATM 300 Ambient Environment Scanning Tunneling Microscope (STM) for atomic- and molecular-resolution imaging of soft biological and polymeric materials under ambient and liquid conditions. The proposed instrument will be housed in the Center for Nano- and Molecular Science and Technology at The University of Texas at Austin (UT-Austin), where it will be accessible 24 hrs a day, 365 days a year, for hands-on materials characterization and experiments conducted by student, postdoctoral, and faculty researchers from multiple colleges and academic departments around campus, as well as to outside academic and industrial users. The RHK STM will complement existing imaging and chemical analysis at UT-Austin by filling an unmet need on our campus for an instrument capable of providing atomic- and molecular-scale resolution of soft materials such as polymers and biological molecules under ambient environmental conditions. This instrument will become a central focus of Army Research Office (ARO) sponsored research in the laboratory of the Principle Investigator, support additional Department of Defense research at UT-Austin, and enhance the teaching mission of the University by training students and postdoctoral researchers in cutting-edge imaging of complex biological and polymeric systems at the frontiers of materials science.

Enter List of papers submitted or published that acknowledge ARO support from the start of the project to the date of this printing. List the papers, including journal references, in the following categories:

(a) Papers published in peer-reviewed journals (N/A for none)

Received Paper

TOTAL:

Number of Papers published in peer-reviewed journals:

(b) Papers published in non-peer-reviewed journals (N/A for none)

Received Paper

TOTAL:

Number of Papers published in non peer-reviewed journals:

(c) Presentations

Number of Presentations: 0.00

Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

Received Paper

TOTAL:

Number of Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

Peer-Reviewed Conference Proceeding publications (other than abstracts):

Received Paper

TOTAL:

Number of Peer-Reviewed Conference Proceeding publications (other than abstracts):

(d) Manuscripts

Received Paper

TOTAL:

Number of Manuscripts:

Books

Received Book

TOTAL:

Received	Book Chapter

TOTAL:

Patents Submitted

Patents Awarded

Awards

Graduate Students

NAME	PERCENT_SUPPORTED

FTE Equivalent:
Total Number:

Names of Post Doctorates

NAME	PERCENT_SUPPORTED

FTE Equivalent:
Total Number:

Names of Faculty Supported

NAME	PERCENT_SUPPORTED

FTE Equivalent:
Total Number:

Names of Under Graduate students supported

NAME	PERCENT_SUPPORTED

FTE Equivalent:
Total Number:

Student Metrics

This section only applies to graduating undergraduates supported by this agreement in this reporting period

The number of undergraduates funded by this agreement who graduated during this period: 0.00

The number of undergraduates funded by this agreement who graduated during this period with a degree in science, mathematics, engineering, or technology fields:..... 0.00

The number of undergraduates funded by your agreement who graduated during this period and will continue to pursue a graduate or Ph.D. degree in science, mathematics, engineering, or technology fields:..... 0.00

Number of graduating undergraduates who achieved a 3.5 GPA to 4.0 (4.0 max scale):..... 0.00

Number of graduating undergraduates funded by a DoD funded Center of Excellence grant for Education, Research and Engineering:..... 0.00

The number of undergraduates funded by your agreement who graduated during this period and intend to work for the Department of Defense 0.00

The number of undergraduates funded by your agreement who graduated during this period and will receive scholarships or fellowships for further studies in science, mathematics, engineering or technology fields: 0.00

Names of Personnel receiving masters degrees

NAME

Total Number:

Names of personnel receiving PHDs

NAME

Total Number:

Names of other research staff

NAME	PERCENT_SUPPORTED

FTE Equivalent:

Total Number:

Sub Contractors (DD882)

Inventions (DD882)

Scientific Progress

A RHK Technology ATM 300 Ambient Environment Scanning Tunneling Microscope (STM) for atomic- and molecular-resolution imaging of soft biological and polymeric materials under ambient and liquid conditions was purchased and installed in December 2013. The instrument is housed in the Center for Nano- and Molecular Science and Technology at The University of Texas at Austin (UT-Austin), where it is accessible 24 hrs a day, 365 days a year, for hands-on materials characterization and experiments conducted by student, postdoctoral, and faculty researchers from multiple colleges and academic departments around campus, as well as to outside academic and industrial users. RHK technicians conducted a lengthy training session for all users, and repeatedly demonstrated the capability for collecting for atomic resolution images on soft substrates. The instrument was subsequently used for extensive investigations in PI Webb's laboratory; first results from this instrument are currently being prepared for publication in leading chemistry journals.

Technology Transfer

Final Report

Defense University Research Instrumentation Program

W911NF-13-1-0318: Multi-Functional Scanning Probe Microscope for Imaging of Soft Surfaces

Dr. Lauren J. Webb, PI

The University of Texas at Austin

Installation and Training: A RHK Technology ATM 300 Ambient Environment Scanning Tunneling Microscope (STM) for atomic- and molecular-resolution imaging of soft biological and polymeric materials under ambient and liquid conditions was purchased and installed in December 2013. The instrument is housed in the Center for Nano- and Molecular Science and Technology at The University of Texas at Austin (UT-Austin), where it is accessible 24 hrs a day, 365 days a year, for hands-on materials characterization and experiments conducted by student, postdoctoral, and faculty researchers from multiple colleges and academic departments around campus, as well as to outside academic and industrial users. A RHK instrument specialist did the initial setup of the RHK STM, including equipment and software installation. Subsequent training of users, also led by the RHK specialist, involved familiarization with equipment components and RHK software, probe tip preparation from Pt/Ir wire, sample preparation and mounting techniques, as well as protocols for approaching and scanning surfaces with the instrument. To verify the capabilities of the STM, several samples were used to confirm lateral and vertical resolution. Using a highly ordered pyrolytic graphite (HOPG) sample, lateral atomic resolution was achieved through confirmation of the hexagonal close packed (hcp) surface structure. For confirmation of the instrument's vertical resolution, an annealed Au(111) surface on mica was imaged, where monatomic step edge height measurements were found to be in close agreement with literature values of ~2.35 Å. Additionally, a user-supplied decanethiol self-assembled monolayer (SAM) on Au sample was imaged, yielding visible confirmation of ordered thiol domains along with resolution of individual terminal methyl groups of the SAM.

Experimental Use: Initial experiments on the STM have involved examining the structure, composition, and stability of peptide-terminated surfaces formed from chemical reaction of a self-assembled monolayer (SAM) of alkane thiols on a gold surface. Although the formation of SAMs on Au surfaces, and subsequent reaction of functional groups in the SAM are both well-understood surface preparation methods, we were interested in whether these two reactions could be done in a one-pot reaction. An integrated approach, in which SAM formation and reaction can be conducted simultaneously, would be an important advance for substrates or materials that cannot withstand prolonged reaction times or chemical conditions. Visualizing the SAM surface for evidence of molecular-level disorder, defects, and damage, is an important characterization tool when comparing to these surfaces to the current standard.

Scanning tunneling microscopy was performed to characterize the topography of a clean gold surface reacted with 0.25 mM azide-terminated alkane thiol, 5 μM peptide, and 15 μM CuCl catalyst, as well as a control sample composed of a decanethiol-terminated SAM exposed to 5 μM peptide and 100 μM CuCl catalyst. The decanethiol control was exposed to such a high concentration of CuCl to ensure that the CuCl concentration range we used does not interfere with SAM formation, which would be apparent with the high-resolution capabilities of STM. The RHK Technology ATM 300 STM was used to obtain high-resolution images of the functionalized surfaces at ambient temperature and pressure. Samples were imaged using a 0.3–

0.5 V bias and a 10 pA tunneling current. STM tips consisted of mechanically cut platinum/iridium wire (80% Pt/20% Ir, Nanoscience). Image processing consisted of using a masked high-pass filter fitting procedure to flatten the image, correct the plane tilt, and remove noise along the fast-scan direction due to low-frequency building vibrations.

Figure 1 shows STM images of the decanethiol control (left panel) and the reacted surface (right panel). The scale bars for both images are 10 nm. The image of the decanethiol control was much smoother than that of the reacted surface, likely due to 70°C temperatures used for these reactions making ordering of the surface occur much more quickly than in the room temperature conditions typically employed. Small, bright features dot the surface and correspond with the width and length dimensions (2 × 3 nm) of the α-helical peptides used in these experiments, similar to our previous STM studies of our peptide-functionalized surfaces. We calculated the peptide surface coverage by determining the fraction of pixels assigned as peptide features from the whole image.

In the control sample, only 5% of the surface was covered with peptides, indicating a small amount of physisorbed peptide on the surface. This is not surprising since the samples created for STM characterization were only rinsed with ethanol. Rinsing with phosphate-buffered saline (PBS) has been shown to reduce the amount of physisorbed proteins on a surface, as the ions in the buffer can compete for adsorption on the surface. However, we were not able to optimize imaging settings to minimize tip-sample interactions with our PBS-rinsed samples and also observed that imaging was less stable in general. Additionally, the peptides are likely to interact more strongly with the decanethiol surface because the peptide is composed of leucine and lysine residues, which end up on opposing sides of the rotational plane of the helical peptide; hydrophobic leucine residues would interact with the methyl-terminated decanethiol surface. In the right panel of Figure 1, the image of the fully reacted surface shows ~78% peptide coverage. Occasional bright features are likely due to α-helical peptides that are attached to the surface through only one of the two propargylglycine residues, resulting in them physically protruding from the surface. It is also likely that additional peptides are physisorbed onto the peptide surface. This visible confirmation of reaction success would not have been possible without the high-resolution capabilities of the RHK STM. These results are being prepared for publication.

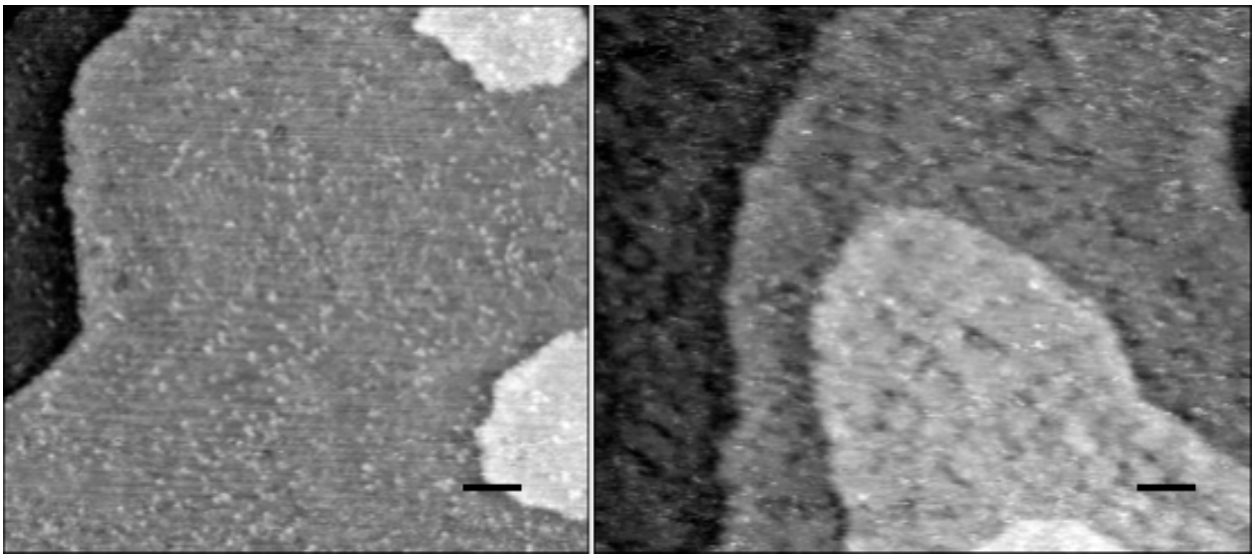

Figure 1. STM images of a control (left) and a peptide-functionalized surface (right). The decanethiol-terminated control surface was exposed to 5 μM peptide and 100 μM CuCl reaction catalyst. The reacted surface was exposed to 5 μM peptide and 15 μM CuCl catalyst. The scale bar is 10 nm.